

# Sorption and Desorption of Cadmium by Different Fractions of Biosolids-Amended Soils

Ganga M. Hettiarachchi,\* James A. Ryan, Rufus L. Chaney, and Cherie M. La Fleur

## ABSTRACT

To evaluate the importance of both the inorganic and organic fractions in biosolids on Cd chemistry, a series of Cd sorption and desorption batch experiments (at pH 5.5) were conducted on different fractions of soils from a long-term field experimental site. The slope of the Cd sorption isotherm increased with rate of biosolids and was different for the different biosolids. Removal of organic carbon (OC) reduced the slope of the Cd sorption isotherm but did not account for the observed differences between biosolids-amended soils and a control soil, indicating that the increased adsorption associated with biosolids application was not limited to the increased OC from the addition of biosolids. Removal of both OC and Fe/Mn further reduced the slopes of Cd sorption isotherms and the sorption isotherm of the biosolids-amended soil was the same as that of the control, indicating both OC and Fe/Mn fractions added by the biosolids were important to the increased sorption observed for the biosolids-amended soil samples. Desorption experiments failed to remove from 60 to 90% of the sorbed Cd. This "apparent hysteresis" was higher for biosolids-amended soil than the control soil. Removal of both OC and Fe/Mn fractions was more effective in removing the observed differences between the biosolids-amended soil and the control than either alone. Results show that Cd added to biosolids-amended soil behaves differently than Cd added to soils without biosolids and support the hypothesis that the addition of Fe and Mn in the biosolids increased the retention of Cd in biosolids-amended soils.

THE NUTRIENTS and organic matter contained in biosolids provide a valuable resource to agriculture, forestry, and remediation of degraded lands. Additionally, biosolids contain varying concentrations of trace elements and organic compounds, which have been the subject of extensive research. Researchers reported that metals added to soils as constituent of biosolids are less phytoavailable than metal salt added to the soil. Further, they found that metal salt added to soils with biosolids are less phytoavailable than metal salts added to soils without biosolids (Brown et al., 1998; Hooda and Alloway, 1993; Bell et al., 1991; Mahler et al., 1987; Singh, 1981; Street et al., 1977; Gaynor and Halstead, 1976; Cunningham et al., 1975a,b). From this body of work, it has been concluded that the addition of biosolids to the soil alters the chemical properties in the soil system. Further, it is apparent that this alteration does

not require large additions of biosolids. The phase or phases responsible for this alteration has and continues to be in dispute. Beckett et al. (1979) postulated the "time-bomb" hypothesis in which it is assumed that the responsible phase is organic and as the organic material decomposes its complexing nature will be lost with a subsequent release of metal to the inorganic system where it will behave as a salt addition to the soil. In contrast, Corey et al. (1987) predicted that biosolids adsorption chemistry is related to inorganic components that control the activity of metals in biosolids-amended soils after reaching saturation of soil metal binding sites. In its development of regulations designed to protect human health and the environment from reasonably anticipated adverse effects of land application of biosolids, the USEPA's reliance on this difference in phytoavailability of metals in soil systems amended with biosolids (USEPA, 1993) intensified the debate. McBride (1995) questioned the long-term safety of this assumption and reiterated the concerns of Beckett et al. (1979). Further, the use of biosolids to remediate metal-contaminated sites (Li et al., 2000) has focused attention on the debate and the long-term efficiency of the treatments with biosolids.

Indirect methods of characterization (e.g., chemical extractions) and theoretical considerations suggest that metals in biosolids exist as soluble, organically complexed, adsorbed forms coprecipitated with Fe, Al, P, and Ca solid phases (Lake et al., 1984; Jing and Logan, 1992). Lake et al. (1984) stated that metals in biosolids are predominantly associated with solid phases and less than 10% of total metals are soluble and/or exchangeable. Li et al. (2001) demonstrated that Cd sorption for biosolids-amended soils was intermediate to biosolids and the control soil and increased with increasing biosolids application rate. Removal of organic carbon (OC) reduced metal sorption for all samples but did not account for the observed differences between biosolids-amended soils and control, indicating that the increased sorption associated with biosolids application was not limited to the increased OC from the biosolids application. However, their study did not directly evaluate the importance of the Fe and Mn fractions for the increased sorption of metals in biosolids-amended soils.

Surfaces of freshly precipitated metal (hydr)oxides such as Fe, Mn, and Al are known to be highly active sites for sorption of most dissolved metal ion species. Trace metal adsorption to Fe and Al oxides has been extensively studied (Hohl and Stumm, 1976; Kinniburgh et al., 1976; Bolland et al., 1977; Benjamin and Bloom, 1981; Kuo and McNeal, 1984; Weesner and Bleam,

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**Abbreviations:** -Fe/Mn, easily reducible iron and manganese removed; -FeO, free iron oxide removed; OC, organic carbon; -OC, organic carbon removed.

**Table 1. Selected properties of soils and biosolids-amended soils (BAS).**

Material	Rate	pH	Organic C	Cd <sub>T</sub> <sup>†</sup>	Mn <sub>T</sub> <sup>†</sup>	Fe <sub>T</sub> <sup>†</sup>	Al <sub>T</sub> <sup>‡</sup>
	Mg ha <sup>-1</sup>		g kg <sup>-1</sup>	mg kg <sup>-1</sup>		%	
Control soil	0	6.6	14.2	0.2	160.1	1.17	0.470
Lime-treated, digested BAS	448	7.0	21.8	0.9	197.0	1.53	0.593
Lime-treated, composted BAS	448	6.8	27.7	1.7	399.6	1.60	0.547
Heat-treated BAS	112	6.6	19.3	3.2	255.7	1.29	1.421

<sup>†</sup> Determined by USEPA Method 3051 (USEPA, 2001). T, total.

<sup>‡</sup> Determined by USEPA Method 3052 (USEPA, 2001). T, total.

1998). As the high specific surface area of amorphous or colloidal iron oxides is expected to result in higher adsorption capacity, Fe oxides have received the greatest attention. Manganese oxides have received less attention in spite of their lower  $\text{pH}_{\text{PZC}}$  and, therefore, high negative surface charge in the pH range generally found in soils. Fresh biologically oxidized and poorly crystallized or amorphous Mn oxides with larger surface areas for adsorption (Birnie and Paterson, 1991; Nelson et al., 1999) could be important in controlling cationic metal concentrations in soils. Biosolids contain high levels of Fe, Mn, and Al. Therefore, it is possible that inorganic components, especially Fe and Mn phases of biosolids, are responsible for controlling the metal availability in biosolids-amended soil systems. If these hypotheses are correct, removal of Fe and Mn fractions should remove a significant portion of the observed enhanced sorption capacity in biosolids-amended soils compared with the control.

To better predict the environmental fate and mobility of contaminants, it is critical to study the desorption behavior as well as the sorption behavior of contaminants in soil systems. It is almost certain that trace metals sorb onto oxides and other soil constituents specifically (chemisorption) and sorption reactions generally show poor reversibility (Sposito, 1989; McBride, 1989). However, it is unclear whether the surface reaction is genuinely irreversible or simply slow in the reverse direction. One explanation for the irreversible nature of metal sorption is that the activation energies for desorption may be much larger than sorption; thus, rates of desorption at normal soil temperatures are likely to be much slower than rates of sorption (McBride, 1989). Another explanation involves the incorporation of metals into the oxides making them unavailable for desorption (true irreversibility).

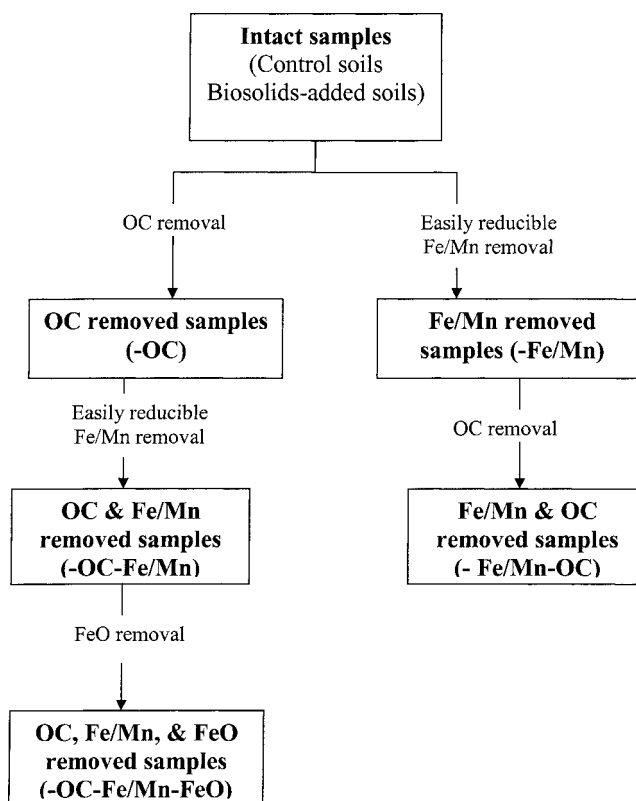
The purpose of this study was to investigate the sorption and desorption of Cd in soils with or without biosolids amendments, and to determine the importance of organic matter and easily reducible Fe and Mn fractions on sorption and desorption in these soils. The resulting information is important to understanding the phase or phases responsible for enhanced metal retention observed in biosolids-amended soils and developing effective strategies for in situ stabilization of toxic metals in soils.

## MATERIALS AND METHODS

Soils samples from a long-term field experiment with different rates and types of biosolids were used in this study. The experimental site was established in 1976 at the Hayden Research facility of the University of Maryland, in conjunction

with the USDA Agricultural Research Center in Beltsville, MD, on a Christiana fine sandy loam (fine, kaolinitic, mesic Typic Paleudult). Samples were taken from control and treated plots receiving a lime-treated, digested biosolids from the Piscataway Treatment Plant in Upper Marlboro, MD; a lime-treated, composted biosolids from the Blue Plains Treatment Plant in Washington, DC; and heat-treated biosolids from Annapolis, MD at application rates of 448, 448, and 112 Mg ha<sup>-1</sup>, respectively. Selected properties of the control soil and biosolids-amended soils are given in Table 1. For more information on this site see Brown et al. (1998).

Soil samples were collected during spring 2001, from the 0- to 15-cm depth (plow layer) of the center area of the field plot for use in this study. Sampling was accomplished with a shovel that was rinsed with 0.01 M HNO<sub>3</sub> followed by a deionized water rinse between plot samples. Each plot sample, collected in kilogram quantities, was placed in labeled 18.9-L (5-gallon) plastic pails. The moist samples were homogenized and sieved using a stainless steel screen with an opening of 2 mm. Subsamples were placed in well-sealed plastic bottles and transferred to the USEPA Center Hill facility, Cincinnati, OH, where they were stored at 4°C until used to prepare soil fractions for the Cd sorption study (Fig. 1).



**Fig. 1. Fractionation scheme used to evaluate the relative contribution of different soil fractions on Cd sorption-desorption.**

### Soil Analysis

Soil pH (1:2 soil to  $H_2O$ ) was measured according to USEPA Method 9045C (USEPA, 2001). Organic carbon content of the samples was measured with a Dohrmann (Santa Clara, CA) DC-190 total organic carbon (TOC) analyzer equipped with Dohrmann Model 183 TOC boat sampler after removal of inorganic C with 0.005 *M* HCl treatment. Soil samples were digested using two methods recommended for total metals: concentrated  $HNO_3$  (USEPA Method 3051; USEPA, 2001) and a combination of concentrated HF and  $HNO_3$  (USEPA Method 3052; USEPA, 2001) in a microwave oven. Total metals in the  $HNO_3$ -digested samples were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Model ICAP 61E; Thermo Elemental, Franklin, MA) or graphite furnace (PerkinElmer HGA-600 with Zeeman 5100 background correction) connected to atomic absorption spectrometry (AAS; Model 5100PC; PerkinElmer, Wellesley, MA) (USEPA Method 6010B; USEPA, 2001); while metals in the HF +  $HNO_3$ -digested samples were analyzed by AAS (Model 5100PC; PerkinElmer) (USEPA Method 7020; USEPA, 2001).

### Organic Carbon Removal

The sodium hypochlorite (NaOCl) method (Shuman, 1983) was chosen over the hydrogen peroxide ( $H_2O_2$ ) method for removal of OC in these materials. The more commonly used  $H_2O_2$  method causes dissolution of Mn oxides (Jackson, 1956) as well as alkaline earth carbonates and phosphates (Anderson, 1963; Lavkulich and Wiens, 1970), whereas the NaOCl procedure permits the removal of OC effectively with minimal destruction to Mn oxides and other inorganic phases (Anderson, 1963). To a 1-g sample (dry weight basis) placed in a 50-mL plastic centrifugal tube, 20 mL of 0.7 *M* NaOCl (adjusted to pH 8.5 with HCl) was added and the resulting solution was heated to 90°C in a water bath for 2 h with occasional mixing. After cooling, the sample was centrifuged and the supernatant was collected. For the solid residue this oxidation procedure was repeated and after the second oxidation step, the soil residue (-OC) was washed thrice for approximately 2 min (each) with 30 mL (each) 0.01 *M*  $Ca(NO_3)_2$  (pH 7.0) to remove the excess NaOCl left in the sample. After each extraction and washing, samples were centrifuged and the supernatant samples were collected. Separate analyses of these extracting and washing solutions for Fe, Mn, and other metals were performed by ICP-AES. The results were then combined to obtain information on Fe and Mn removed by the extraction procedure. Washed residue (-OC) was used for sorption-desorption experiments. The organic carbon content of the solid residue (-OC) was determined using a TOC analyzer as described before.

### Easily Reducible Iron and Manganese Removal

The Tessier et al. (1979) procedure was used for removal of easily reducible Fe and Mn. One gram of sample (dry weight basis) was weighed into 50-mL centrifuge tubes and 20 mL of 0.04 *M*  $NH_2OH \cdot HCl$  in 25% HOAc was added. The resulting mixture was placed in a hot water bath maintained at 96°C and digested for 6 h with occasional mixing. After digestion, the sample was centrifuged and the supernatant collected. The solid residue was washed, and extracting and washing solutions were analyzed separately as mentioned previously. Washed residue (-Fe/Mn) was used for sorption-desorption experiments. Additionally, the OC content of the solid residue

(-Fe/Mn) was determined using a TOC analyzer as described before to determine the propensity of this extracting procedure to extract OC.

### Free Iron Oxides Removal

Some soil samples contained significant amounts of free Fe oxides that could not be extracted by the Tessier et al. (1979) procedure. For these samples, a modified Kunze and Dixon (1986) procedure (citrate-bicarbonate-dithionite, CBD) for the removal of free Fe oxides was used. Twenty milliliters of 0.3 *M* sodium citrate and 2.5 mL of 0.5 *M*  $NaHCO_3$  were added to a 1-g sample (dry weight basis) placed in a 50-mL plastic centrifugal tube. The suspension was heated to 80°C in a water bath, and then 0.5 g of  $Na_2S_2O_4$  was added. The mixture was stirred constantly for 1 min and occasionally during the next 14 min of digestion at 80°C. After digestion, samples were centrifuged and residue (-FeO) was washed, and the extracting and washing solutions were analyzed as described previously.

### Organic Carbon Removal followed by Iron and Manganese Removal (and Vice Versa)

In addition to removal of OC or Fe/Mn, samples were treated to remove OC followed by removal of Fe/Mn (-OC-Fe/Mn), or removal of Fe/Mn followed by removal of OC (-Fe/Mn-OC). The control and lime-treated composted biosolids-amended soil samples were treated to remove free Fe oxides after removal of OC and Fe/Mn (-OC-Fe/Mn-FeO). After each extraction procedure, solid residue was washed, and the extracting and washing solutions were analyzed as mentioned previously. The washed residue was used for the sorption-desorption experiments.

### Cadmium Sorption

Intact soil samples (whole), the -OC sample, the -Fe/Mn sample, the -OC-Fe/Mn sample, the -Fe/Mn-OC sample, and the -OC-Fe/Mn-FeO sample were suspended in 20 mL of 0.01 *M*  $Ca(NO_3)_2$ . Solution pH in the suspension was adjusted to  $pH\ 5.5 \pm 0.1$  using 0.01 *M* NaOH or 0.01 *M*  $HNO_3$ . The suspension volume was adjusted to 25 mL with 0.01 *M*  $Ca(NO_3)_2$  and shaken on a platform shaker with a reciprocal movement at 140 rpm. After the pH stabilized (within  $\pm 0.1$  units) and had been maintained at  $pH\ 5.5 \pm 0.1$  for 24 h, suspensions were centrifuged and the supernatant was filtered through a 0.45- $\mu m$  filter. Solutions were stored in a refrigerator at 4°C until the analysis. The sample was resuspended in 20 mL of 0.01 *M*  $Ca(NO_3)_2$ , and Cd standard solution [ $Cd\ as\ Cd(NO_3)_2 \cdot 6H_2O$ ] was quantitatively added to give four known Cd concentrations (12, 24, 48, and 72  $\mu g$  of Cd). The pH of the suspension was adjusted to 5.5 with 0.01 *M* NaOH or 0.01 *M*  $HNO_3$  and the volume was adjusted to 25 mL with 0.01 *M*  $Ca(NO_3)_2$ . All the sample tubes were sealed and shaken on a platform shaker at 140 rpm for 48 h at  $23 \pm 1^\circ C$ . Approximately 2 to 4 h after the shaking started the suspension pH was measured. If pH was not within  $\pm 0.1$  units of the desired pH level, additional pH adjustment was made. The volume of acid or base used during the adjustment was recorded and added to the total volume for use in final calculation. After a minimum of 48 h of equilibration time or at least 24 h after the pH had stabilized, the pH was checked and verified to be within  $\pm 0.1$  units of the desired pH. The sample was centrifuged and the clear supernatant filtered through a 0.45- $\mu m$  filter. If the pH was not within  $\pm 0.1$  pH units of the desired pH level, the sample was discarded, and the procedure was repeated. Solutions were stored in a refrigerator at 4°C until

the analysis. The analysis for Cd was performed by ICP-AES according to USEPA Method 6010B (USEPA, 2001). The amount of Cd sorbed was calculated as the difference between the known initial Cd concentration and final Cd concentration. Solid residue from the sorption experiment was used for the desorption experiments.

### Cadmium Desorption

Moist solid residue (approximately 1 g, dry weight basis) from the sorption experiments was suspended in 20 mL 0.01 M  $\text{Ca}(\text{NO}_3)_2$ . The pH of the suspension was adjusted to  $5.5 \pm 0.1$  using 0.01 M  $\text{HNO}_3$  and 0.01 M  $\text{NaOH}$ . The volume was adjusted to 25 mL using 0.01 M  $\text{Ca}(\text{NO}_3)_2$ . All the sample tubes were sealed and shaken on a platform shaker at 140 rpm for 48 h at  $23 \pm 1^\circ\text{C}$ . About 2 to 4 h after the shaking started, the suspension pH was checked. If pH was not within  $\pm 0.1$  units of the desired pH level, additional adjustment of pH was made. After a minimum of 48 h of equilibration time or at least 24 h after the pH had stabilized, the pH was checked to verify that it was within  $\pm 0.1$  units of the desired pH. The sample was centrifuged and the clear supernatant was filtered through a 0.45- $\mu\text{m}$  filter. If the pH was not within  $\pm 0.1$  pH units of the desired pH level, the sample was discarded, and the procedure was repeated. The solid residue was resuspended in 20 mL 0.01 M  $\text{Ca}(\text{NO}_3)_2$  and the desorption experiment as previously described was repeated at least one more time. The analysis for Cd was performed by ICP-AES according to USEPA Method 6010B (USEPA, 2001).

## RESULTS AND DISCUSSION

### Effects of Extracting Solutions

In this study, selective extraction procedures were used to determine the relative significance of the different components in controlling Cd sorption-desorption. However, as the possibility of extracting solution components other than the target components cannot be excluded, the effects of the different extracting solutions on other soil components were measured (Table 2).

The NaOCl extracting solution effectively removed OC from soil samples (Table 2). Remaining OC may be (i) interlayered between other soil constituents; (ii) nondegradable, plastic-like compounds as mentioned by Li et al. (2001); or (iii) thin layers surrounding other soil constituents. Its reactivity in the system is assumed to be negligible. Even though NaOCl treatment was intended to selectively remove OC, it removed additional components. For example, NaOCl treatment removed 19 to 31% of the total soil Mn, and <1 to 2.4% of the total soil Fe and <1 to 2% of the total soil Al

from tested soils. These extracted phases either were in association with OC or existed as inorganic phases. These phases as well as OC removed with the NaOCl extracting solution may have been responsible for metal retention in the intact sample.

The  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in the 25% acetic acid (HOAc) extracting procedure removed 84 to 100% of the total soil Mn, suggesting that most Mn in these soils can be extracted by this extracting solution (Table 2). However, Fe removal ranged between 14 to 39% of the total soil Fe, indicating that most of soil Fe existed in forms that this extracting procedure could not remove. Frampton and Reisenauer (1978) reported that the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% acetic acid is only capable of extracting amorphous Fe oxides, though it is proven to be an effective extracting solution for Mn from soils (Shuman, 1982). It extracts as much Mn as most of the other extractions used for the extraction of various Fe compounds. Our observations are in agreement with Shuman (1982).

Besides the target materials, Fe and Mn, the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% HOAc extraction also removed 5 to 12% of the total soil Al and <1 to 54% of the total soil OC. The NaOCl treatment followed by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% HOAc treatment generally increased the amounts of Al removed considerably (7–35% of the total soil Al). This was not the case for the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% HOAc treatment followed by the NaOCl treatment. These results indicate that there were some Al compounds in these soils that could only be removed by the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% HOAc treatment after treatment to remove OC.

### Cadmium Sorption

Effects of biosolids addition on Cd sorption at pH 5.5 are shown in Fig. 2. These typical sorption isotherms illustrate the linearity of Cd sorption for a soil or fraction of soil, within the range of Cd concentrations used in this experiment. In fact, the isotherm was still linear at an order of magnitude higher solution concentration (data not shown). The coefficients of determination for a sample ranged from 0.94 to 0.99. As illustrated by these isotherms, application of biosolids increased the slope of the sorption isotherm and the increase was different for the different biosolids. These observations are in agreement with previous Cd adsorption studies conducted in our laboratory with different biosolids-

**Table 2.** Effects of selective extractions on removal of organic carbon (OC), iron, manganese, and aluminum from soils.

Treatment†	0.7 M NaOCl at pH 8.5				0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc				0.7 M NaOCl at pH 8.5 followed by 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc				0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc followed by 0.7 M NaOCl at pH 8.5			
	OC	Fe	Mn	Al	OC	Fe	Mn	Al	OC	Fe	Mn	Al	OC	Fe	Mn	Al
	% removal															
Control	~90	<1	19	2	<1	14	84	11	~90	16	63	32	~90	13	76	10
Lime-treated, digested BAS	~90	<1	20	2	5	15	92	12	~90	16	68	35	~90	14	92	11
Lime-treated, composted BAS	~90	2.4	31	2	27	21	100	8	~90	23	71	28	~90	20	100	8
Heat-treated BAS	~90	<1	24	<1	54	39	100	5	~90	39	100	7	NA‡	NA	NA	NA

† Biosolids-amended soils.

‡ Not applicable.

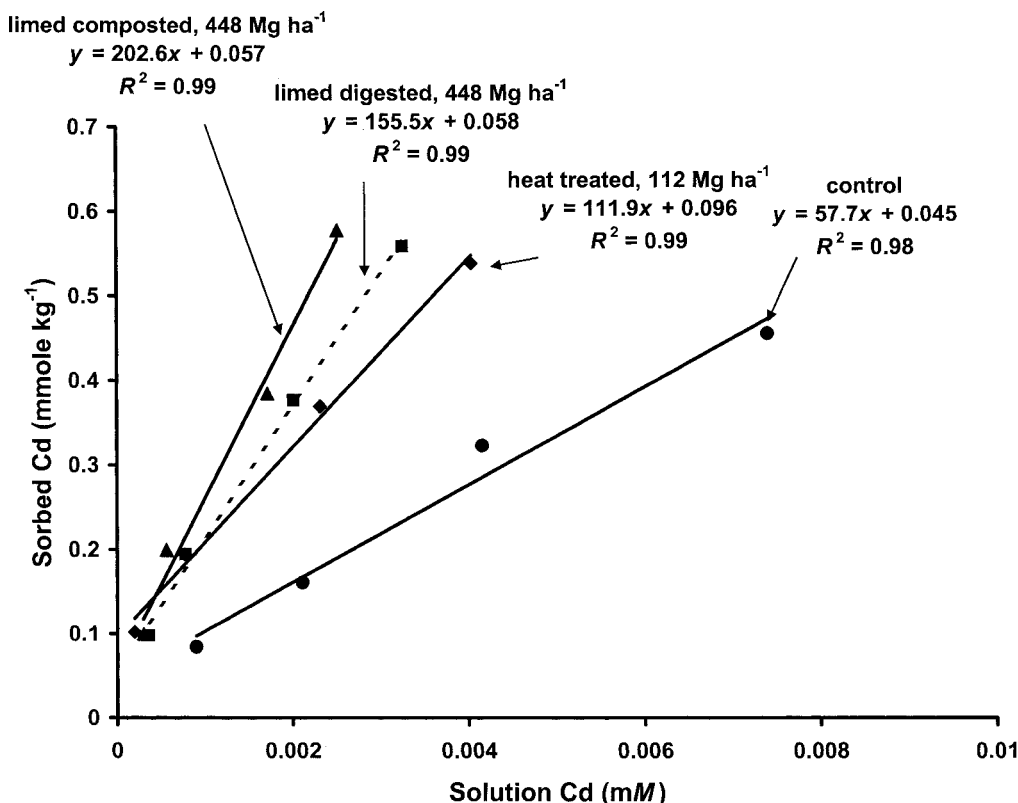


Fig. 2. Effects of biosolids on Cd sorption at pH 5.5 in 0.01 M  $\text{Ca}(\text{NO}_3)_2$  solution.

amended soils (Li et al., 2001) and support the hypothesis that the addition of biosolids to soil alters the chemical properties of the soil system. We believe that the addition of biosolids adds extra adsorptive phases to soil systems and therefore alters its adsorptive characteristics.

The slopes of the Cd sorption isotherm for heat-treated (Annapolis), lime-treated composted, and lime-treated digested biosolids were 1.93, 3.51, and 2.69 times greater than the control soil, respectively (Fig. 2). The slope of the Cd sorption isotherm for the lime-treated composted biosolids was higher than that of the lime-treated digested biosolids at equivalent loading rates ( $448 \text{ Mg ha}^{-1}$ ) and that of the heat-treated (Annapolis) biosolids applied at  $112 \text{ Mg ha}^{-1}$  is lowest. Assuming that the increase in the Cd sorption isotherm is dependent on rate of biosolids application, the heat-treated (Annapolis) biosolids would have the greater slope if the application rate was  $448 \text{ Mg ha}^{-1}$ . Theorizing identical application rates ( $448 \text{ Mg ha}^{-1}$ ) for the biosolids, their slope order would be the same as the order of Fe concentrations reported by Chaney et al. (1982) (8.3, 4.1, and 2.5% for the heat-treated [Annapolis], lime-treated composted, and lime-treated digested biosolids materials, respectively), suggesting that the increase in slope can be associate with Fe application rate.

The slope of the Cd sorption isotherm decreased significantly because of OC removal for both the control soil sample and the biosolids-amended soil sample suggesting that OC is important for the adsorption of Cd

by these soils (Fig. 3). However, removal of the OC fraction did not result in the biosolids-amended soil sample behaving like the control soil. In other words, enhanced Cd sorption due to biosolids application was still apparent after removing the OC (approximately 90%) for lime-treated composted biosolids-amended soil. This indicates that both the OC fraction and the inorganic fraction are responsible for enhanced Cd sorption observed in the biosolids-amended soils. A similar trend was observed for other tested biosolids-amended soils (data not shown) and agrees with the observations of Li et al. (2001) on the importance of the inorganic fraction of biosolids to the increased Cd sorption of biosolids-amended soil. This observation complements those of Mahler et al. (1987) and Brown et al. (1998), which indicated that either inorganic phases in biosolids or recalcitrant OC are responsible for maintaining low plant availability in biosolids-amended soils.

Removal of easily reducible Mn and/or Fe oxides resulted in a significant reduction in the slope of the Cd sorption isotherm in both the control and the biosolids-amended soils, suggesting that this inorganic fraction is important to Cd adsorption (Fig. 4). However, removal of the easily reducible Fe and Mn fractions did not cause the biosolids-amended sample to behave like the control soil. Similar results were observed for other biosolids-amended soils, indicating that other fractions as well as the easily reducible Fe and Mn fraction are responsible for the enhanced Cd sorption observed in the biosolids-amended soils.

Of the biosolids-amended soils tested in this study,

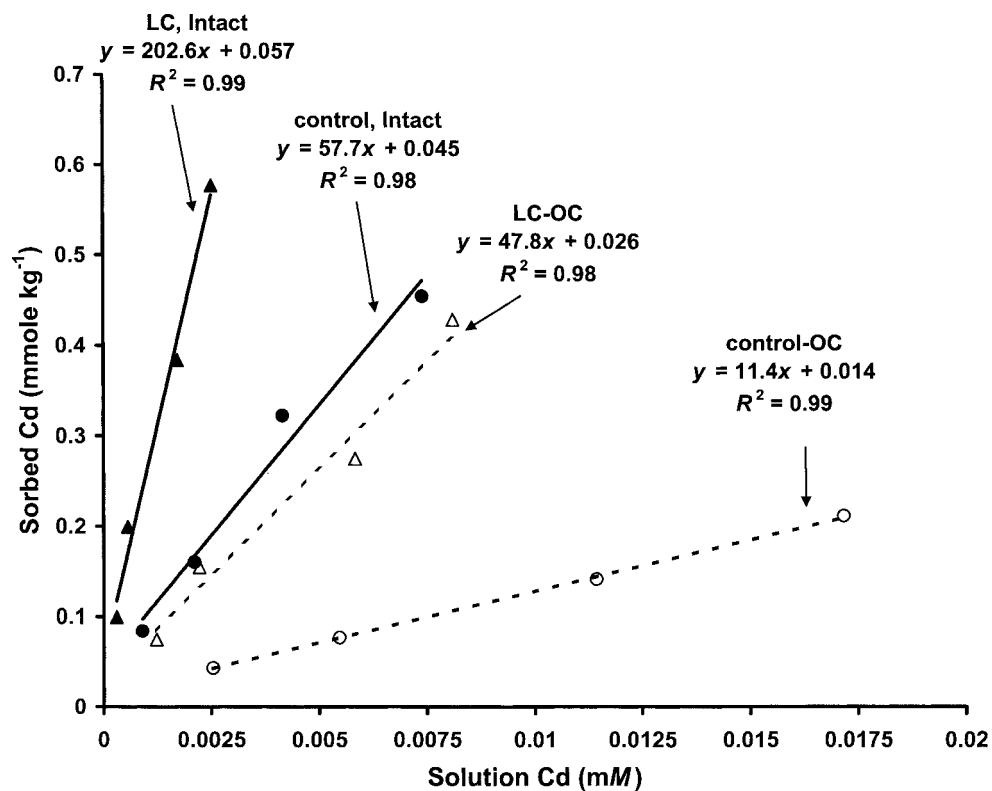


Fig. 3. Effects of biosolids and organic carbon removal on Cd sorption at pH 5.5 in 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> solution. LC, limed digested; OC, organic carbon.

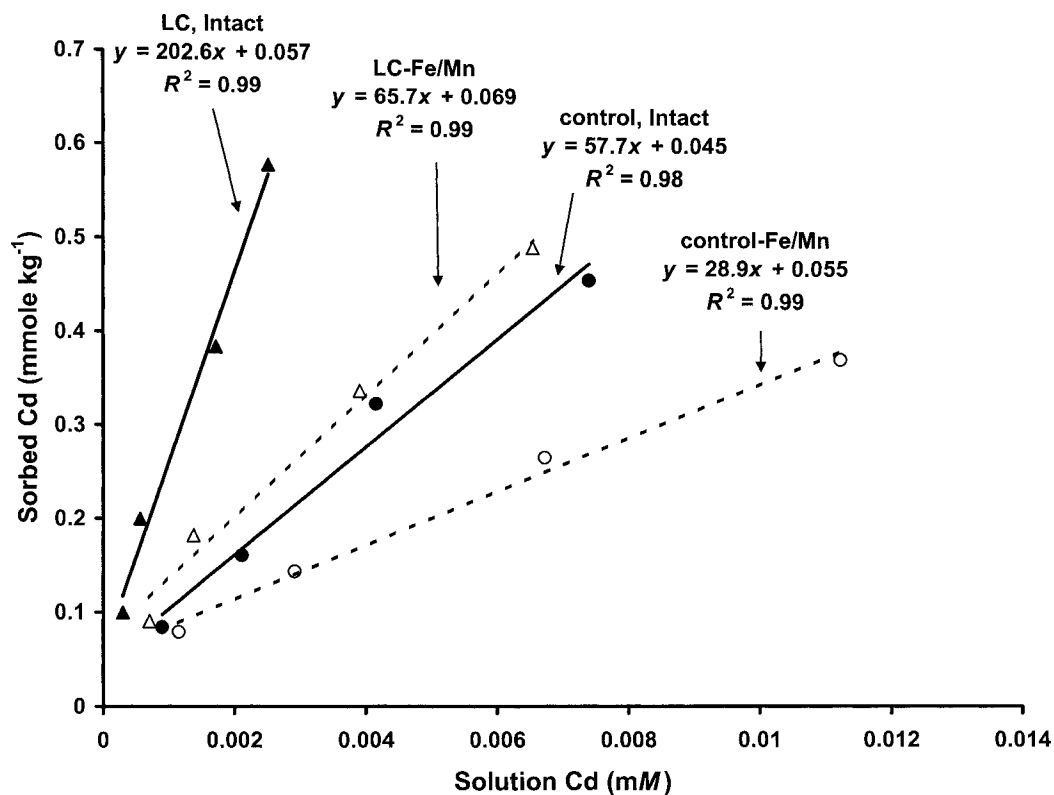


Fig. 4. Effects of biosolids and easily reducible Fe/Mn removal on Cd sorption at pH 5.5 in 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> solution. LC, limed digested.

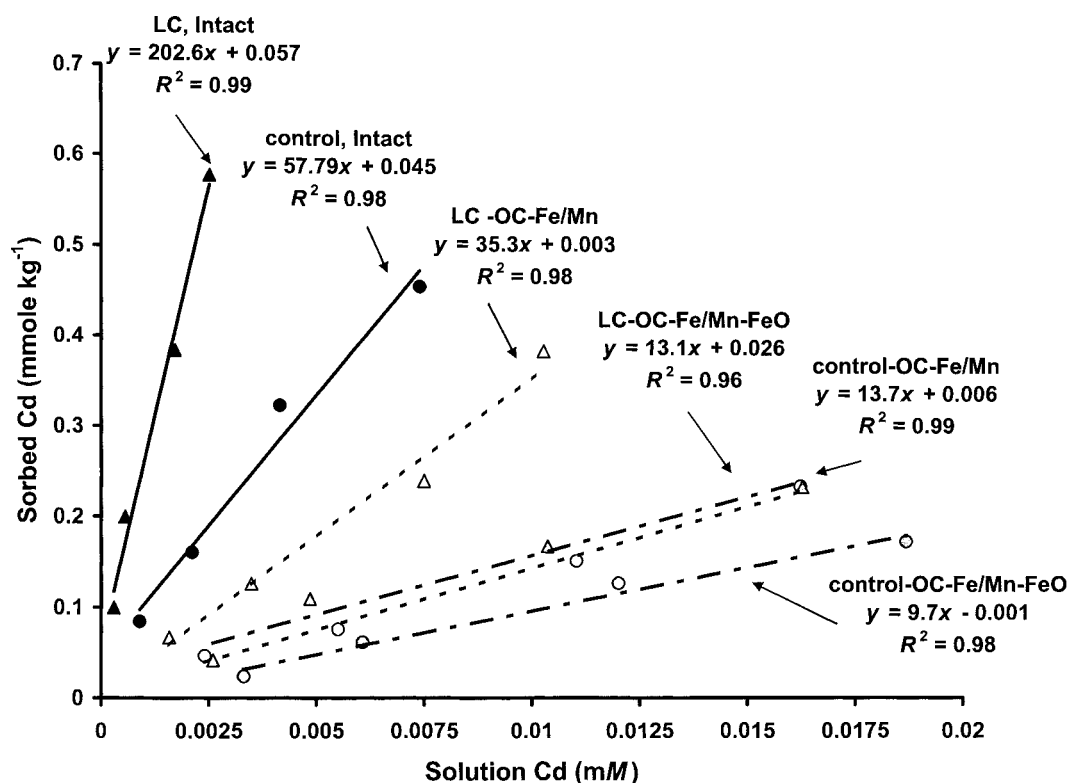


Fig. 5. Effects of biosolids, easily reducible Fe/Mn, organic carbon, and Fe oxide removal on Cd sorption at pH 5.5 in 0.01 M  $\text{Ca}(\text{NO}_3)_2$  solution. LC, limed digested; OC, organic carbon.

removal of OC followed by removal of easily reducible Fe and Mn (or vice versa) was sufficient to remove the enhanced Cd sorption observed in the biosolids-amended soils compared with the control soil except for the lime-treated composted biosolids-amended soil sample (only data for lime-treated composted biosolids-amended soil sample are shown) (Fig. 5). Chao and Zhou (1983) reported that acidified hydroxylamine hydroxide dissolves almost all Mn and amorphous Fe oxides; however, the dissolution of crystalline Fe oxides by this extracting solution is minimal. As Fe extractable by hydroxylamine hydrochloric procedure removed less than 31% of the total Fe in any of these soils (Table 2), it seems that these soils had crystalline Fe oxides or Fe associated with clay minerals. The citrate–bicarbonate–dithionite procedure (CBD procedure; Mehra and Jackson, 1960) is the standard method for removal of free Fe oxides (both amorphous and crystalline) with a minimal destructive action to the clay minerals (Kunze and Dixon, 1986). Lime-treated composted biosolids-amended soil was subjected to the CBD procedure. The hydroxylamine hydrochloric procedure removed approximately 21% of the total Fe from this biosolids-amended soil while the CBD procedure removed nearly 60% of the remaining Fe from the system. As shown in Fig. 5, the differences between the Cd sorption isotherm for the control and the lime-treated composted biosolids-amended soil was further reduced and almost disappeared, implying that lime-treated composted biosolids contained significant amounts of crystalline Fe oxides that are capable of retaining added Cd. However, X-ray

diffraction (XRD) analysis of lime-treated composted biosolids sample failed to show any evidence of the presence of crystalline Fe oxides. It is well known that the direct identification of solid forms of many elements is not always possible with XRD, because only crystalline materials present at concentrations  $\geq 10$  to 20 g  $\text{kg}^{-1}$  can be detected (Ma et al., 1994). X-ray absorption near edge spectroscopy (XANES) studies (data not shown) revealed that the majority of Fe in the lime-treated composted biosolids had mixed oxidation states of +2 and +3 (magnetite-like) and an oxidation state of +3 (goethite-like).

Disappearance of increased Cd sorption isotherms in biosolids-amended soils compared with the control soil after removing OC and easily reducible Mn and Fe (plus other free Fe oxides for the case of lime-treated composted biosolids-amended soil) indicate that not only OC but also Fe and Mn are important in controlling Cd in the soil solution and, therefore, its subsequent plant uptake. These observations are in agreement with long-term experimental studies in which the OC added by biosolids equilibrated to background soil OC content and the change in phytoavailability of metals caused by biosolids application was still present (Mahler et al., 1987; Brown et al., 1998).

### Cadmium Desorption

The results from the desorption experiments for the highest Cd sorbed soil samples for the control and two different biosolids-amended soils are shown in Fig. 6.

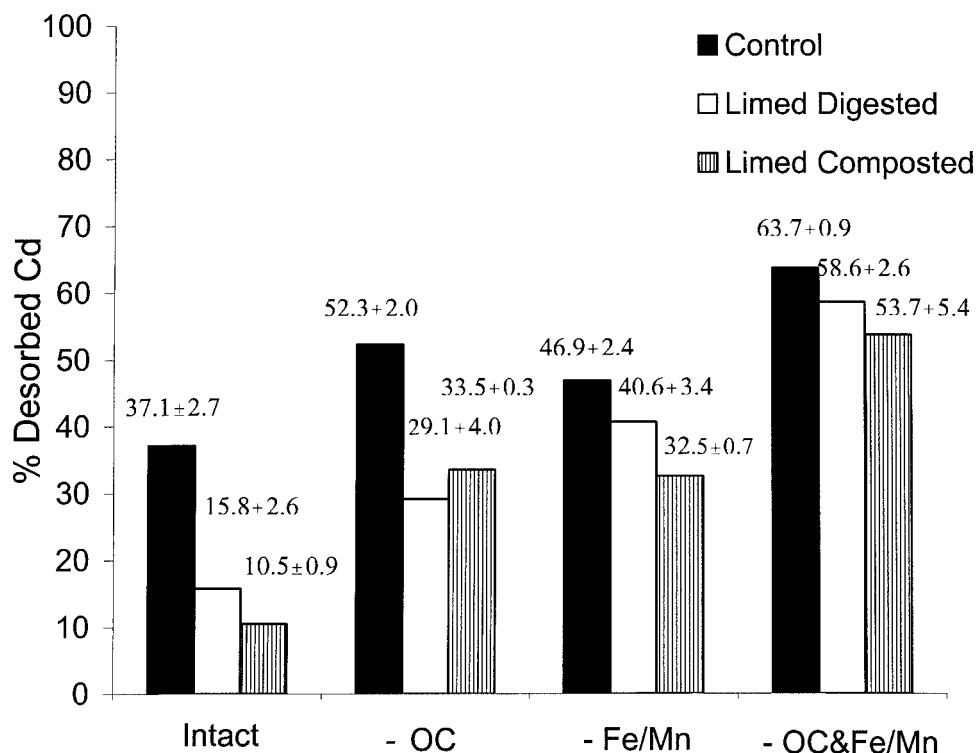


Fig. 6. Effects of removal of different fractions from soils with or without biosolids on Cd desorption at pH 5.5 in 0.01 M  $\text{Ca}(\text{NO}_3)_2$  solution.

Desorption experiments were repeated twice and the duration of a single desorption experiment was approximately 2 d. These desorption experiments were conducted using the same background electrolyte as the sorption experiments [0.01 M  $\text{Ca}(\text{NO}_3)_2$  at pH 5.5]. Many researchers conduct desorption experiments using either organic chelators (such as ethylenediamine tetraacetic acid) or acidic desorbing solutions. Despite all the other important information offered from these desorption experiments, they do not provide the information on desorption behavior in terms of a irreversible reaction in which the desorption conditions are the same as sorption (Strawn and Sparks, 2000).

To make comparisons, the desorption data were converted to percent Cd desorbed by dividing the total amount of Cd desorbed at the end of two consecutive desorption experiments by the total amount of added Cd sorbed by each sample. Since the amounts of Cd recovered in the desorption experiments are smaller than Cd removed from the solution, in the sorption experiment the desorption reactions are incomplete. This is true for all the samples regardless of the treatment (Fig. 6) and regardless of the sorbed Cd concentration (data not shown). This observation can be considered as “apparent hysteresis.” However, it does not verify that the Cd is irreversibly bound to these materials. It is important to point out that samples were desorbed for only 4 d and during this time period the true equilibrium may not have been achieved due to slow desorption reactions. Desorption may have a larger activation energy compared with adsorption; therefore, rates of desorption at normal soil temperatures are likely to be much slower than rates of sorption (McBride, 1989).

It should be noted that not only Cd sorption but also Cd desorption characteristics of biosolids-amended soils are different from the control soil. Figure 6 shows that a substantial proportion of Cd sorbed by biosolids-amended soils cannot be readily desorbed. For example, in the case of intact samples (whole soil), nearly 37.1% of the sorbed Cd was recovered from the control sample whereas only 15.8 and 10.5% were recovered from lime-treated digested and lime-treated composted biosolids-amended soil, respectively. The removal of OC did not cause the biosolids-amended soils to behave like the control sample, indicating that not only the OC fraction but also the inorganic fraction are responsible for the increased “apparent hysteresis” observed in biosolids-amended soils. Effectiveness of Fe and Mn removal in reducing “apparent hysteresis” was different for lime-treated composted and lime-treated digested biosolids-amended soil. The removal of Fe and Mn appeared to be more important than the removal of OC in removing the differences observed in the desorption characteristics between the lime-treated digested biosolids-amended and control soils (Fig. 6). It has been accepted that the trace metals sorb onto metal oxides by chemisorption showing poor reversibility (Sposito, 1989; McBride, 1994). One explanation noted earlier for the irreversible nature of metal sorption by oxides is that the activation energies for desorption may be much larger than sorption; thus, rates of desorption at normal temperatures are likely to be much slower than rates of sorption. Another explanation involves the incorporation of metals into the oxides, making them unavailable for desorption (true irreversibility). Further, increasing contact time between sorbent and metals may

further decrease a metal's ability to desorb from the sorbent (Hogg et al., 1993; Backes et al., 1995). Sorption followed by diffusion of adsorbed ions within the solid oxide material has been proposed as a possible reason for decreased metal desorption with time (Barrow, 1986; Barrow et al., 1989). Therefore, it is reasonable to assume that metals associated with oxides in biosolids-amended soils may be more difficult to desorb compared with the added sorbed Cd in these sorption–desorption experiments. Neither OC removal nor Fe and Mn removal treatments were able to remove the differences between the desorption characteristics of the control and lime-treated composted biosolids-amended soil. As expected, removal of both fractions was more effective in removing those differences than either alone for lime-treated composted biosolids-amended soil. This indicates that increased “apparent hysteresis” in biosolids-amended soils is related to both OC and Fe and Mn fractions. Strawn and Sparks (2000) studied the effects of soil organic matter (SOM) on sorption and desorption behavior of Pb in two soils by treating the soil with sodium hypochlorite to remove the SOM fraction, revealing that removal of SOM plays an important role in decreasing the hysteresis (incomplete or slow desorption reactions) observed in Pb desorption experiments. However, in their study, attempts were not made to observe the importance of Fe and Mn fractions on desorption of Pb.

In this study, our calculations were based on the assumption that all sorbed Cd was from added sorbed Cd in the sorption experiments. The Cd in soils before the sorption experiments should also be considered. This would be more significant for biosolids-amended soils compared with the control soil. If initial Cd had been included, then the differences observed between the control and the biosolids-amended soils would have been greater than reported here; however, that would not change our conclusions. This study provides clear evidences Fe and Mn oxide retention and immobilization of Cd by biosolids.

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